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Supplementary Information

For

Straightforward Catalyst/Solvent-free Iodine-Mediated Living Radical Polymerization of Functional Monomers Driven by Visible Light Irradiation

Xiaodong Liu, Lifen Zhang,* Zhenping Cheng* and Xiulin Zhu

Suzhou key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China.

Experimental section

Materials. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, M_n = 500 g mol^{-1}, Aldrich), 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%, Wako Pure Chemical, Japan) and glycidyl methacrylate (GMA, TCI, > 95.0%, GC) were passed through an alumina column to remove the inhibitor. Methyl methacrylate (MMA), benzyl methacrylate (BnMA) and 2-hydroxyethyl methacrylate (HEMA) were all purchased from Sigma-Aldrich, and were purified by passing through a neutral alumina column before use. 2-Cyanopropyl iodide (CP-I) (99%, TCI (contract service)) was used as received. *N*,*N*-dimethylformamide (DMF), poly(ethylene glycol) (PEG200, M_n = 200 g mol^{-1}) and all other chemicals were obtained from Shanghai Chemical Reagents Co. Ltd and were used as received unless mentioned.

Procedure for bulk polymerization of DMAEMA. A typical bulk polymerization procedure for the molar ratio of $[\text{DMAEMA}]_0 : [\text{CP-I}]_0 = 100 : 1$ was shown as follows: a mixture was obtained by adding DMAEMA (1.0 mL, 5.93 mmol), CP-I (6.74 μL, 0.059 mmol) to a dried ampoule. The mixture was thoroughly degassed by at least three freeze–pump–thaw cycles to eliminate the dissolved oxygen in the reaction system, and then flame-sealed; afterwards it was transferred into LED illumination environment to polymerize under stirring at rt. After the desired polymerization time, the ampoule was then transferred into a dark environment and aliquots were withdrawn using syringes. Subsequently the monomer conversion was determined by ^{1}H NMR using $CDCl_3$ as the solvent, and the number-average molecular weight ($M_{n,\text{GPC}}$) and molecular weight distribution (M_w/M_n) values were analyzed by GPC. The initiator concentration was varied with respect to the target degree of polymerization (DP), while the monomer volume was kept constant in the polymerization system.

Procedure for bulk polymerization of PEGMA or GMA. Detailed procedures were similar to bulk polymerization of DMAEMA.

Procedure for bulk polymerization under sunlight irradiation. Bulk polymerizations under natural sunlight irradiation were conducted on the windowsill of the testing laboratory of polymer chemistry and physics department in Suzhou University. The reaction equipment and the polymerization system were placed on the windowsill of building and directly irradiated by sunlight. The maximum reaction temperatures were measure to be near 29 °C in the mid-afternoon. Data were collected on May 12th, 2016, from 10 a.m. to 4 p.m.

Typical "One-Pot" Chain Extension of PGMA. GMA (0.5 mL, 3.67 mmol), and CP-I (4.16 μL, 0.037 mmol) were added to a 5 mL ampoule equipped with a magnetic stirrer bar. Next, the ampoule was sealed with a rubber stopper, deoxygenated with four freeze-vacuum-thaw cycles, and purged with argon. The reaction was allowed to proceed with stirring under blue LED irradiation at 25 °C for 6 h. As the system has a certain viscosity but without any solidify, a reaction mixture sample used for analysis was collected by using an airtight syringe and purging the side arm of the reactor with argon. Degassed monomer GMA (2.0 mL, 14.66 mmol) was then added to the ampoule under argon by a syringe, and at the same time excessive gas owing to reduced system space was also eliminated through another syringe. The reaction mixture was irradiated upon a blue LED exposure at $\lambda_{\max}$ = 464 nm under magnetic stirring for 10 h. The monomer conversion was determined by ^{1}H NMR spectroscopy, and the number-average molecular weight ($M_{n,\text{GPC}}$) and molecular weight distribution (M_w/M_n) values were determined by GPC.

Characterizations. The number average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) values of the resulting polymers were determined using a TOSOH-HLC-8320 gel permeation chromatograph (GPC) equipped with a refractive index detector (Waters 2414), using TSK gel Super AWM-H columns (4.6 mm I.D. × 15 cm × 2) with measurable molecular weights ranging from 10^3 to 10×10^5 g mol^{-1}. In characterization processes of PPEGMA, PGMA, PMMA and PBnMA, THF was used as the eluent at a flow rate of 0.35 mL min^{-1} at 40 °C. The GPC samples were injected by using a TOSOH plus autosampler, and were calibrated with PMMA standards obtained from TOSOH. In characterization processes of PHEMA and PDMAEMA, DMF + 0.01 mol L^{-1} LiBr was used as an eluent at a flow rate of 0.6 mL min^{-1} operated at 40 ^oC. A TOSOH HLC-8320 gel permeation chromatograph (GPC) equipped with a refractive index detector (TOSOH), using TSKgel guardcolumn SuperAW-H and TSKgel SuperAWM-H × 2 with measurable molecular weight ranging from 1×10^3 to 1×10^6 g mol^{-1} was used. GPC samples were injected using a TOSOH plus autosampler and calibrated with polystyrene (PS) standards purchased from TOSOH. The ^{1}H NMR spectra of the obtained polymers were recorded on a Bruker 300 MHz nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard at ambient temperature. Matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF MS) were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). The compound *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, +98%) dissolved in $CHCl_3$ (20 mg mL^{-1}) was served as the matrix.

Table S1. Polymerizations of 2-(dimethylamino)ethyl methacrylate (DMAEMA).[a]

Entry	**Monomer**	**Light source**	**$[M]_0/[I]_0$**	**Time (h)**	**Conv.**[b] **(%)**	**$M_{n,th}$**[c] **(g/mol)**	**$M_{n,GPC}$**[d] **(g/mol)**	**M_w/M_n**[d]
1	DMAEMA	Blue LED	100/1	4.5	> 99	15760	14170	1.31
2	DMAEMA	Blue LED	200/1	4	73.1	23180	21510	1.26
3	DMAEMA	Blue LED	400/1	5	61.0	38550	44520	1.36
4	DMAEMA	Green LED	100/1	27	65.1	10430	10690	1.29
5	DMAEMA	Purple LED	100/1	2	68.1	10900	10650	1.28
6	DMAEMA	Purple LED	200/1	3	71.7	22740	23870	1.32
7	DMAEMA	White LED	100/1	3.5	71.7	11470	11100	1.28
8	DMAEMA	White LED	200/1	4	87.0	27550	28550	1.53

[a] Polymerization conditions: $[DMAEMA]_0:[CP\text{-}I]_0$ = 100:1, 200:1 or 400:1, $V_{monomer}$ = 1.0 mL, irradiated by LED light at room temperature. [b] Determined by ^{1}H NMR. [c] Calculated based on conversion, $M_{n,th} = M_{CP\text{-}I} + [Monomer]_0/[CP\text{-}I]_0 \times M_{monomer} \times$ conversion%). [d] Determined by GPC in DMF, based on linear PS as calibration standards.

Table S2. Polymerizations of poly(ethylene glycol) methyl ether methacrylate (PEGMA).[a]

Entry	Monomer	Light source	$[M]_0/[I]_0$	Time (h)	Conv.[b] (%)	$M_{n,th}$[c] (g/mol)	$M_{n,GPC}$[d] (g/mol)	M_w/M_n[d]
1	PEGMA	Blue LED	50/1	6	63.3	16020	14120	1.10
2	PEGMA	Blue LED	100/1	12	70.6	35500	31080	1.13
3	PEGMA	Blue LED	200/1	24	56.6	56800	43040	1.24
4	PEGMA	White LED	50/1	8	57.3	14520	13340	1.08
5	PEGMA	White LED	100/1	20	71.5	35950	33250	1.11
6	PEGMA	Green LED	50/1	30	75.0	18950	18230	1.08
7	PEGMA	Green LED	100/1	44	78.8	39600	35870	1.14
8	PEGMA	Purple LED	50/1	8	72.1	18220	15840	1.14
9	PEGMA	Purple LED	100/1	10	27.3	13850	11500	1.16

[a]Polymerization conditions: $[\text{PEGMA}]_0$:$[\text{CP-I}]_0$ = 50:1, 100:1 or 200:1, V_{monomer} = 1.0 mL, irradiated by LED light at room temperature. [b]Determined by ^{1}H NMR. [c]Calculated based on conversion, $M_{n,th} = M_{\text{CP-I}} + [\text{Monomer}]_0/[\text{CP-I}]_0 \times M_{\text{monomer}} \times$ conversion%). [d]Determined by GPC in THF, based on linear PMMA as calibration standards.

Table S3. Polymerizations of glycidyl methacrylate (GMA) under blue LED irradiation.[a]

Entry	Monomer	Light source	$[M]_0/[I]_0$	Time (h)	Conv.[b] (%)	$M_{n,th}$[c] (g/mol)	$M_{n,GPC}$[d] (g/mol)	M_w/M_n[d]
1	GMA	Blue LED	100/1	5	51.9	7570	6960	1.05
2	GMA	Blue LED	100/1	10	91.4	13190	12930	1.07
3	GMA	Blue LED	200/1	5	57.3	16490	15540	1.04
4	GMA	Blue LED	300/1	5	55.0	23650	20740	1.03
5	GMA	Blue LED	400/1	5	55.6	31810	27980	1.05
6	GMA	Blue LED	600/1	12	92.2	78830	57180	1.17
7	GMA	Blue LED	800/1	6	54.5	62170	46369	1.13
8	GMA	Blue LED	800/1	12	91.4	104140	70800	1.23

[a]Polymerization conditions: $[\text{GMA}]_0$:$[\text{CP-I}]_0$ = 100:1, 200:1, 300:1, 400:1, 600:1 or 800:1, V_{monomer} = 1.0 mL, irradiated by LED light at room temperature. [b]Determined by ^{1}H NMR. [c]Calculated based on conversion, $M_{n,th} = M_{\text{CP-I}} + [\text{Monomer}]_0/[\text{CP-I}]_0 \times M_{\text{monomer}} \times$ conversion%). [d]Determined by GPC in THF, based on linear PMMA as calibration standards.

Table S4. Polymerizations of glycidyl methacrylate (GMA) under purple or white LED irradiation.[a]

Entry	Monomer	Light source	$[M]_0/[I]_0$	Time (h)	Conv.[b] (%)	$M_{n,th}$[c] (g/mol)	$M_{n,GPC}$[d] (g/mol)	M_w/M_n[d]
1	GMA	Purple LED	200/1	5	62.5	17960	16810	1.05
2	GMA	Purple LED	300/1	5	65.5	28130	23490	1.04
3	GMA	Purple LED	400/1	5	64.0	36590	32440	1.07
4	GMA	Purple LED	600/1	8	85.3	72950	71570	1.30
5	GMA	Purple LED	800/1	8	87.9	100150	92650	1.44
6	GMA	White LED	100/1	5	68.1	9880	9280	1.04
7	GMA	White LED	200/1	5	65.6	18850	14850	1.03
8	GMA	White LED	300/1	5	64.0	27490	22890	1.03
9	GMA	White LED	400/1	5	59.7	34140	25690	1.04
10	GMA	White LED	600/1	12	90.5	77380	51070	1.16
11	GMA	White LED	800/1	12	81.3	92650	78320	1.22

[a]Polymerization conditions: $[\text{GMA}]_0$:$[\text{CP-I}]_0$ = 100:1, 200:1 300:1, 400:1, 600:1 or 800:1, V_{monomer} = 1.0 mL, irradiated by LED light at room temperature. [b]Determined by ^{1}H NMR. [c]Calculated based on conversion, $M_{n,th} = M_{\text{CP-I}} + [\text{Monomer}]_0/[\text{CP-I}]_0 \times M_{\text{monomer}} \times$ conversion%). [d]Determined by GPC in THF, based on linear PMMA as calibration standards.

Table S5. Polymerizations of functional monomers under sunlight irradiation.[a]

Entry	Monomer	Light source	$[M]_0/[I]_0$	Time (h)	Conv.[b] (%)	$M_{n,th}$[c] (g/mol)	$M_{n,GPC}$[d] (g/mol)	M_w/M_n[d]
1	PEGMA	Sunlight	50/1	2.5	61.2	15500	14480	1.10
2	PEGMA	Sunlight	50/1	3	76.9	19420	18260	1.10
3	PEGMA	Sunlight	100/1	2	53.0	26700	22210	1.14
4	PEGMA	Sunlight	100/1	3	73.7	37050	32390	1.29
5	PEGMA	Sunlight	150/1	3	62.9	47370	37580	1.38
6	DMAEMA	Sunlight	100/1	3	~100	15920	14510[e]	1.34[e]
7	DMAEMA	Sunlight	200/1	3	99.4	31450	31210[e]	1.57[e]
8	GMA	Sunlight	100/1	3	63.2	9180	8760	1.06
9	GMA	Sunlight	200/1	3	69.3	19900	22470	1.04
10	GMA	Sunlight	400/1	4	70.1	40050	46950	1.19
11	GMA	Sunlight	600/1	4	68.1	58280	65710	1.30
12	GMA	Sunlight	800/1	6	56.2	64110	92400	1.44

[a]Polymerization conditions: $[\text{Monomer}]_0$:$[\text{CP-I}]_0$ = 50:1, 100:1, 150:1, 200:1, 400:1, 600:1 or 800:1, V_{monomer} = 1.0 mL, at room temperature irradiation by sunlight or LED light. [b]Determined by ^{1}H NMR. [c]Calculated based on conversion, $M_{n,th} = M_{\text{CP-I}} +$

[Monomer]$_0$/[CP-I]$_0$ × M_{monomer} × conversion%). [d]Determined by GPC in THF, based on linear PMMA as calibration standards. [e]Determined by GPC in DMF, based on linear PS as calibration standards.

Table S6. Polymerizations of other monomers (MMA, BnMA, HEMA).[a]

Entry	**Monomer**	**Light source**	**$[M]_0/[I]_0$**	**Time (h)**	**Conv.[b] (%)**	**$M_{n,th}$[c] (g/mol)**	**$M_{n,GPC}$ (g/mol)**	**M_w/M_n**
1	MMA	Blue LED	100/1	18	9.37	1130	1140[d]	1.05[d]
2	BnMA	Blue LED	100/1	18	19.9	3700	4950[d]	1.19[d]
3	HEMA	Purple LED	100/1	7.5	60.2	8030	9990[e]	1.57[e]
4	HEMA	Purple LED	200/1	12	37.1	9850	11510[e]	1.56[e]

[a]Polymerization conditions: [Monomer]$_0$:[CP-I]$_0$ = 100:1 or 200:1, V_{monomer} = 1.0 mL, irradiated by LED light at room temperature. [b]Determined by ^{1}H NMR. [c]Calculated based on conversion, $M_{n,th}$ = $M_{\text{CP-I}}$ + [Monomer]$_0$/[CP-I]$_0$ × M_{monomer} × conversion%). [d]Determined by GPC in THF, based on linear PMMA as calibration standards. [e]Determined by GPC in DMF, based on linear PS as calibration standards.

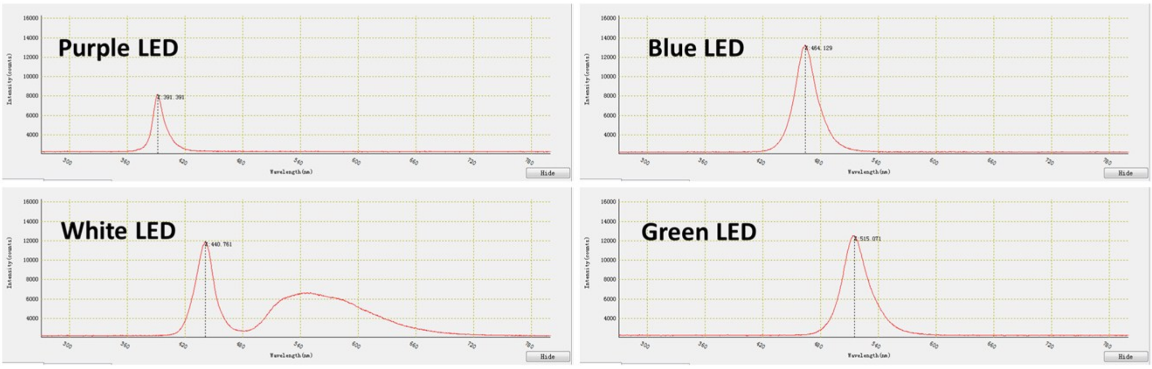


Fig. S1 Emission spectra of LEDs. The peaks are 390 ± 30 nm for the purple LED, 464 ± 40 nm for the blue LED, 515 ± 40 nm for the green LED with the breadths of the distribution are given by half of the full width at half maximum. The emission wavelength for the white LED was 400-720 nm, λ_{max} = 440, 540 nm. The emission intensities changes with the variation of distance of the light source to the inductive sensor.

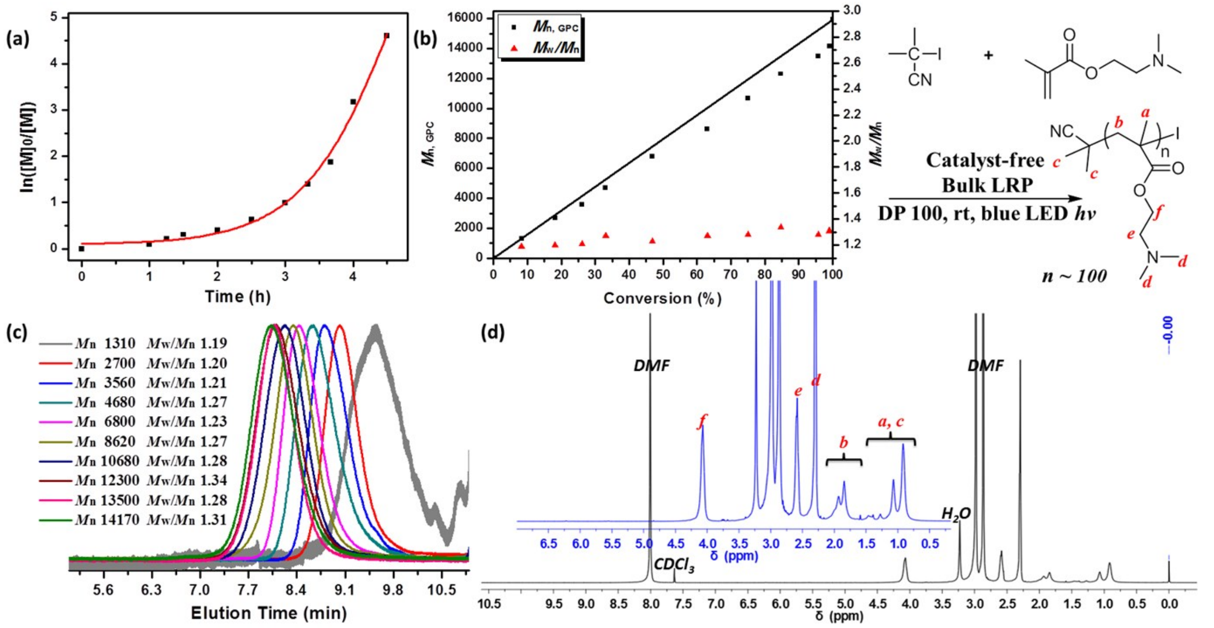


Fig. S2 ln([M]$_0$/[M]) as a function of time (a), number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) *versus* monomer conversion (b) and GPC curves (c) for photoinduced catalyst-free bulk LRP of DMAEMA. Polymerization conditions: [DMAEMA]$_0$:[CP-I]$_0$ = 100:1, V_{DMAEMA} = 1.0 mL, samples were irradiated by a blue LED at rt; (d) ^{1}H NMR spectra of PDMAEMA ($M_{n,GPC}$ = 14170 g mol^{-1}, M_w/M_n = 1.31) obtained by photo-induced catalyst-free bulk LRP under conditions of [DMAEMA]$_0$:[CP-I]$_0$ = 100:1 for 4.5 h.

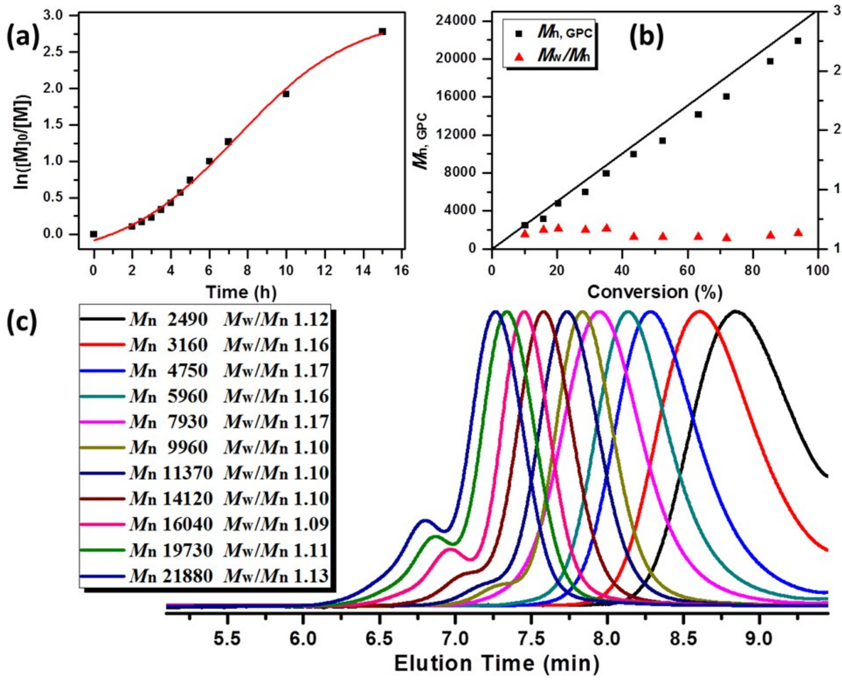


Fig. S3 ln([M]$_0$/[M]) as a function of time (a), number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) *versus* monomer conversion (b) and GPC curves (c) for photo-induced catalyst-free bulk LRP of PEGMA. Polymerization conditions: [PEGMA]$_0$: [CP-I]$_0$ = 50:1, V_{PEGMA} = 1.0 mL; samples were irradiated by a blue LED at rt.

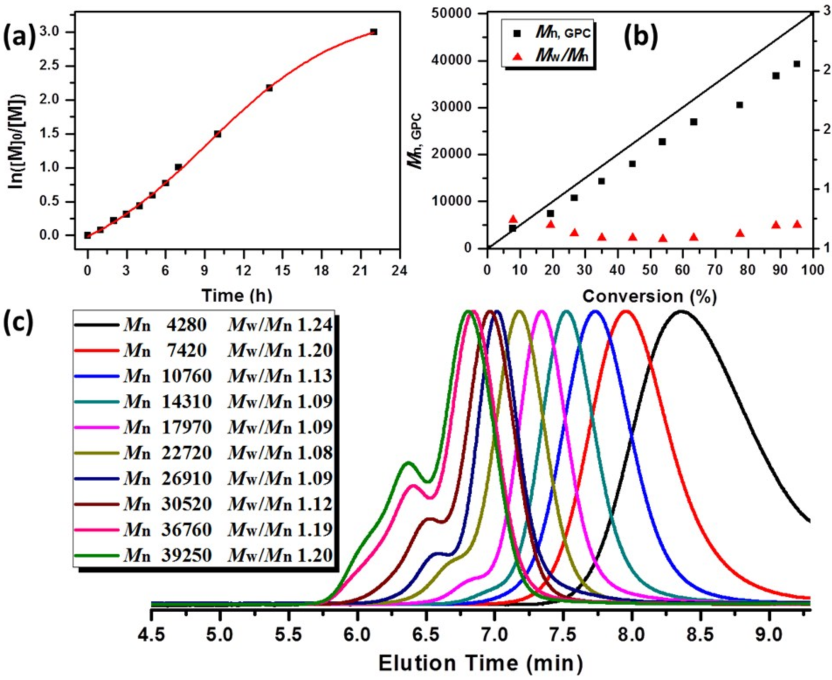


Fig. S4 ln([M]$_0$/[M]) as a function of time (a), number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) *versus* monomer conversion (b) and GPC curves (c) for photoinduced catalyst-free bulk LRP of PEGMA. Polymerization conditions: [PEGMA]$_0$: [CP-I]$_0$ = 100:1, V_{PEGMA} = 1.0 mL; samples were irradiated by a blue LED at rt.

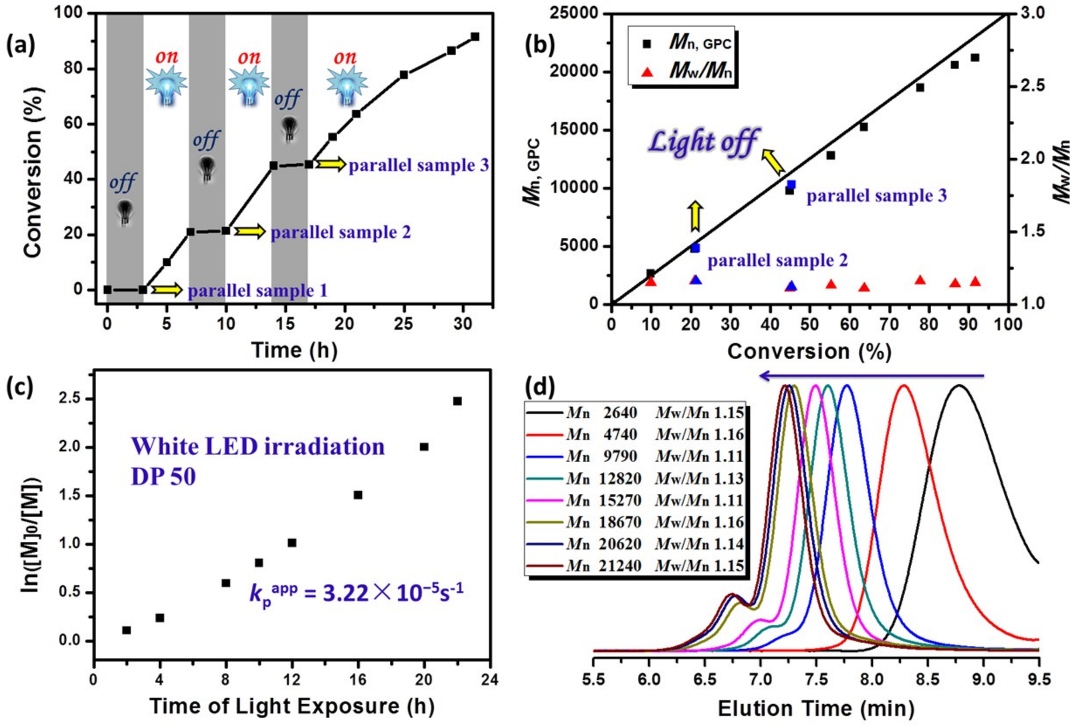


Fig. S5 (a) Plot of monomer conversion *versus* time demonstrating the effect of white light on the control over polymerization propagation through repeated "on-off" cycling of irradiation (white regions) and light source removal (shaded regions); number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) *versus* monomer conversion (b), ln([M]$_0$/[M]) as a function of exposure time (c), and GPC curves (d) for photoinduced catalyst-free LRP of PEGMA in the "on-off" light irradiation experiments. Polymerization conditions: [PEGMA]$_0$:[CP-I]$_0$ = 50:1, V_{PEGMA} = 1.0 mL; samples were irradiated by a white LED at rt.

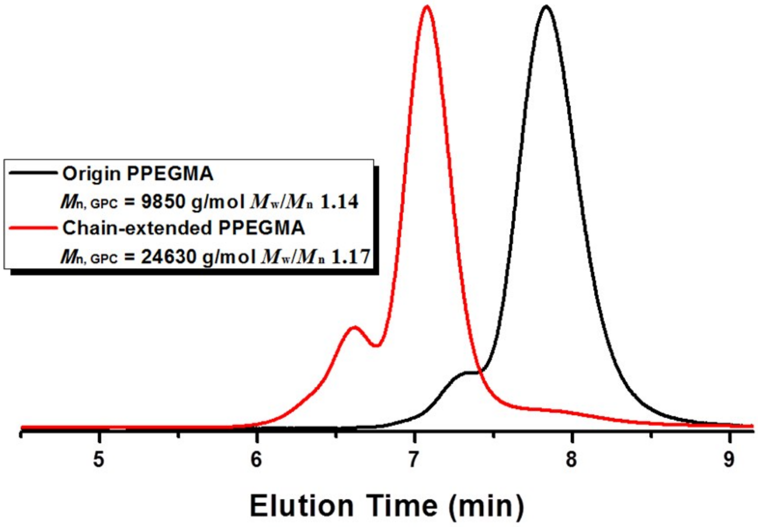


Fig. S6 GPC chromatograms before and after chain extension using PEGMA ($M_{n,GPC}$ = 9850 g mol^{-1}, M_w/M_n = 1.14) prepared by catalyst-free bulk LRP of PEGMA under blue LED irradiation of $[PEGMA]_0:[CP\text{-}I]_0$ = 20:1 for 6 h as the macroinitiator.

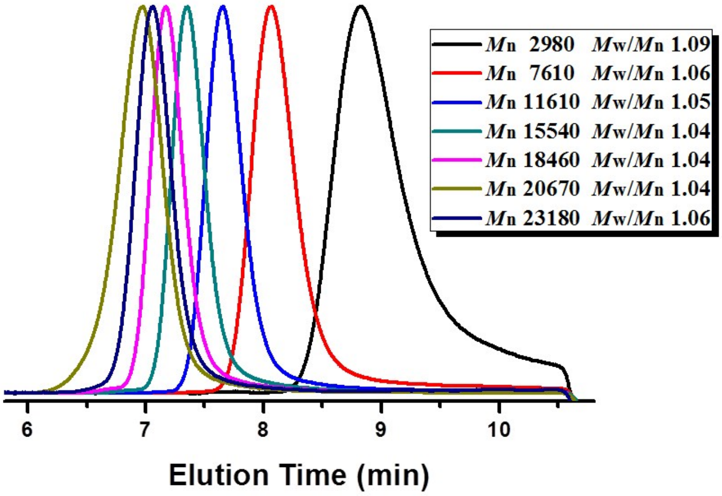


Fig. S7 GPC curves for photoinduced catalyst-free bulk LRP of GMA. Polymerization conditions: $[GMA]_0:[CP\text{-}I]_0$ = 200:1, V_{GMA} = 1.0 mL; samples were irradiated by a blue LED at rt.

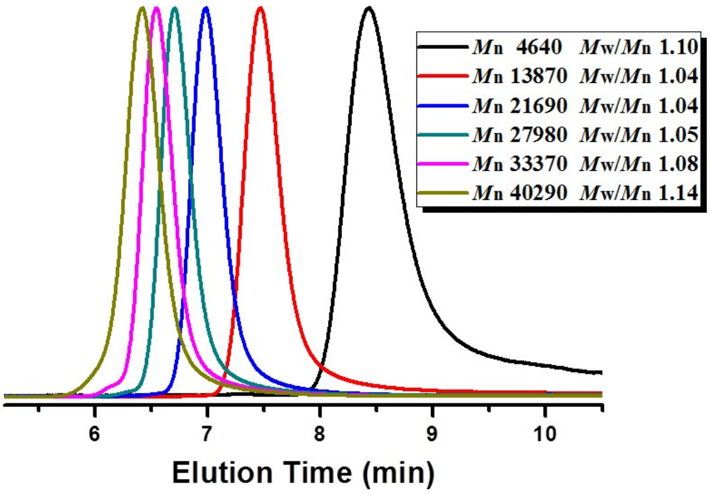
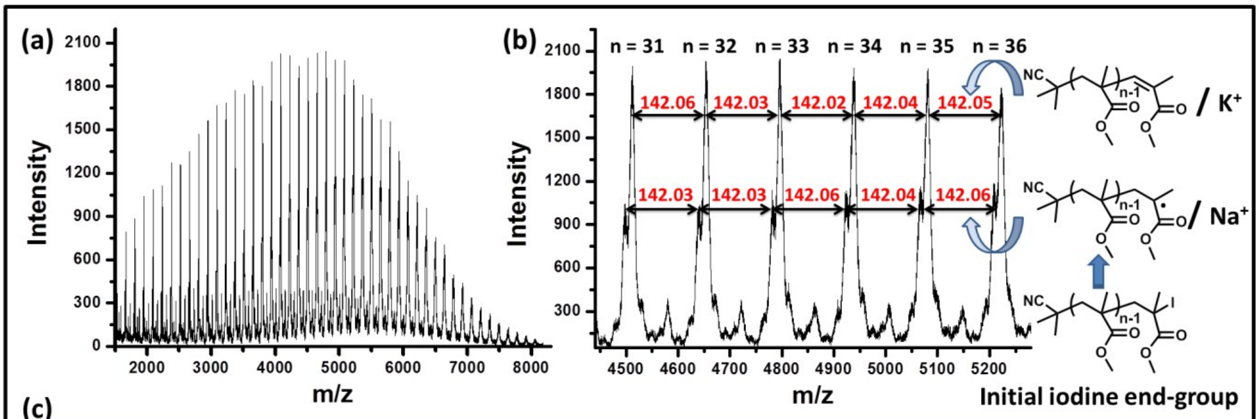


Fig. S8 GPC curves for photoinduced catalyst-free bulk LRP of GMA. Polymerization conditions: $[GMA]_0$:$[CP\text{-}I]_0$ = 400:1, V_{GMA} = 1.0 mL; samples were irradiated by a blue LED at rt.



(c)

Species	*m/z*	n = 31	n = 32	n = 33	n = 34	n = 35	n = 36
CP-(GMA)$_n^{\cdot}$, Na$^+$	$M_{n,cal}$	4496.999	4639.062	4781.125	4923.188	5065.251	5207.314
	$M_{n,exp}$	4497.336	4639.365	4781.397	4923.461	5065.497	5207.558
CP-(GMA)$_{n-1}$-GMA$^=$, K$^+$	$M_{n,cal}$	4511.965	4654.028	4796.091	4938.154	5080.217	5222.280
	$M_{n,exp}$	4511.418	4653.481	4795.507	4937.522	5079.564	5221.612

Fig. S9 (a) MALDI-TOF-MS in the linear mode of PGMA ($M_{n,GPC}$ = 4130 g mol^{-1}, M_w/M_n = 1.11, Conv. = 9.1%) obtained by visible light induced catalyst-free bulk LRP of GMA under white LED irradiation of $[GMA]_0$: $[CP\text{-}I]_0$ = 300 : 1 for 2 h. (b) Enlargement of the MALDI-TOF-MS from m/z 4440 to 5280. (c) Polymeric species with the theoretical ($M_{n,cal}$) and the experimental ($M_{n,exp}$) *m/z* values from the MALDI-TOF-MS spectrum, respectively. Species were labeled as *α*-end group-(BMA)$_{\text{chain length}}$-*ω*-end group, "GMA$^=$" indicates unsaturated GMA end group.

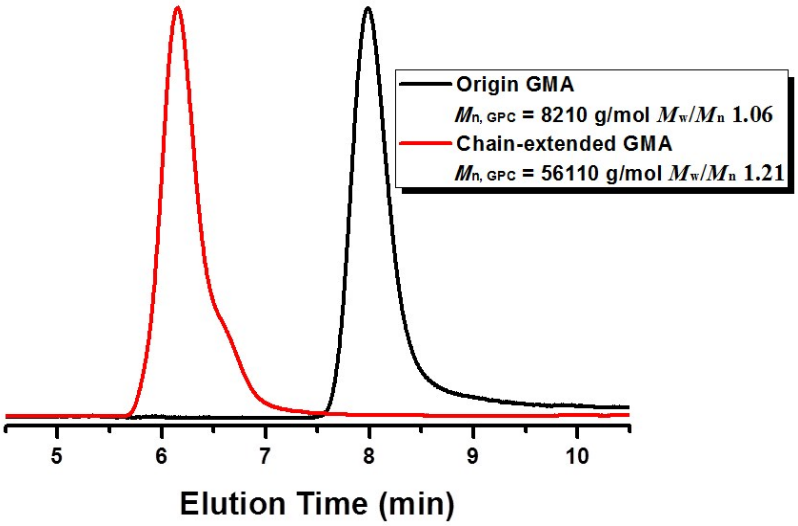


Fig. S10 GPC chromatograms before and after chain extension using GMA ($M_{n,GPC}$ = 8210 g mol^{-1}, M_w/M_n = 1.06) prepared by catalyst-free bulk LRP of GMA under blue LED irradiation of $[GMA]_0:[CP\text{-}I]_0$ = 100:1 for 6 h as the macroinitiator.

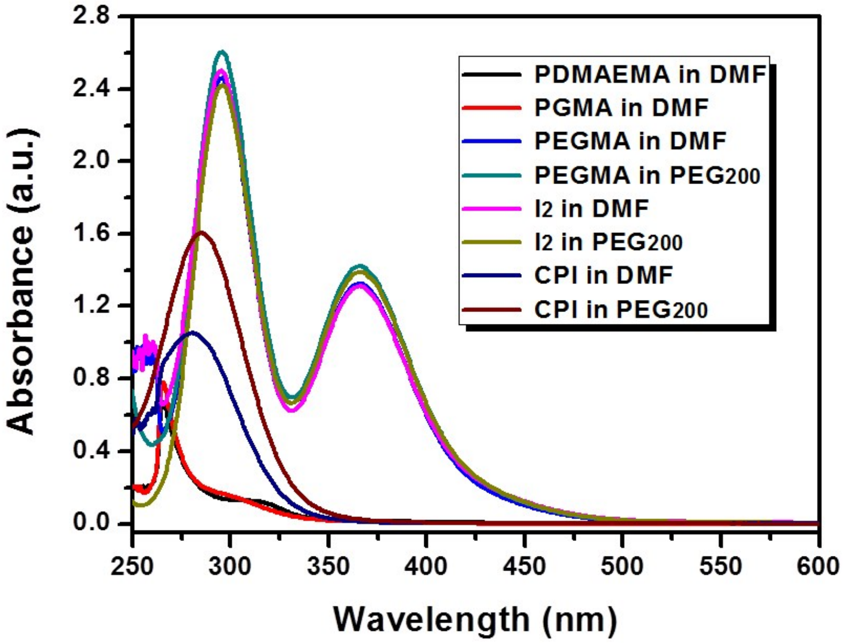


Fig. S11 UV-Vis absorption spectra of various polymerization systems prepared under blue LED irradiation; the polymerization systems were diluted with DMF or PEG200 and calculated by the original initiator (CP-I) concentration before measurement (PDMAEMA: 0.58 mM, DP 200, 4 h, 73.1% Conv.; PGMA: 0.58 mM, DP 200, 8 h, 81.8% Conv.; PEGMA: 0.58 mM, DP 50, 7h, 71.9% Conv.; I_2: 0.08 mM; CP-I: 2.82 mM).

Supplemental instruction

Recently, visible light mediated polymerization emerging as a novel and facile polymerization technique has garnered much attention due to its switched "on" and "off" states with temporally and spatially control. To demonstrate this unique feature, the component proportion was fixed to $[\mathrm{PEGMA}]_0$:$[\mathrm{CP\text{-}I}]_0$ = 50:1, and the polymerizations were conducted at room temperature under white LED light with "off/on" light switching cycles. As shown in Fig. S5, 3 h of dark environment provided no polymer initially, and then the mixture of PEGMA and CPI was exposed to a white LED light reaching 9.9% conversion (M_n = 2640 g mol^{-1}, M_w/M_n = 1.15) and 20.9% conversion (M_n = 4740 g mol^{-1}, M_w/M_n = 1.16) for 2 h and 4 h, respectively. After this time, the reaction was kept in the dark for another 3 h. GPC and ^{1}H NMR analysis indicated that dark period contributed tiny molecular weight (M_n = 4820 g mol^{-1}, M_w/M_n = 1.16) and monomer conversion variations (21.3%). Continued irradiation of the polymerization system led to regenerated polymer growth. Another 4 h of light exposure provided a polymer with M_n = 9790 g mol^{-1} and M_w/M_n = 1.11 at 44.9% conversion. By simple tuning the light "off" and "on", the system could be feasibly stopped and restarted again. The polymerization proceeded smoothly, reaching 91.6% conversion in 22 h of exposure time (M_n = 21240 g mol^{-1} and M_w/M_n = 1.15). General survey of light switching regulation indicated that the plot of $M_{n,\mathrm{GPC}}$ *versus* monomer conversion provided a linear relationship, and the molecular weight distributions during polymerization remained narrow (M_w/M_n =1.11 ~ 1.16) (Fig. S5b), which suggested a controlled/"living" polymerization process. The plot of $\ln([M]_0/[M])$ increased as exposure time with a slight dynamic accelerating feature (Fig. S5c). Thus temporally controlled synthesis of PPEGMA with cycles of "off-on" light switching demonstrated that irradiation was an essential element for the initiation and regulation of this photoinduced catalyst-free bulk LRP, and no polymerization was observed when the light was removed while the polymerization proceeded as expected upon re-exposure to light.

Samples of PPEGMA could also be used as an efficient macroinitiator for chain extension of PEGMA under blue LED light irradiation (Fig. S6). The polymerizations were initiated at 25 °C by CPI in the presence of PEGMA ($[\mathrm{PEGMA}]_0$:$[\mathrm{CP\text{-}I}]_0$ = 20:1, V_{PEGMA} = 1.0 mL) to generate the macroinitiator (M_n = 9850 g mol^{-1} and M_w/M_n = 1.14) with monomer conversion of 91.1 %. "One-Pot" chain extension was conducted upon addition of new PEGMA monomers (V_{PEGMA} = 2.0 mL) under argon by a syringe. Relatively high monomer conversion (82.5%) at the end of whole polymerization process was confirmed *via* ^{1}H NMR, from which we can extrapolate that 74.9% of monomers were consumed in the chain extension stage. The evolution of the GPC molecular weight distributions of the chain extension of PEGMA reveals that the molecular weight of the model PEGMA homopolymer was significantly increased ($M_{n,\mathrm{GPC}}$ = 24630 g mol^{-1}) and molecular weight distributions remains narrow (M_w/M_n = 1.17). However, a perceivable molecular weight shoulder in GPC elution curve reflected a loss of livingness which was attributed to dead polymer chains formed during radical-coupling (RC) reactions.

According to the mechanism of the reversible complexation mediated polymerization (RCMP), we can infer that iodine radical ($\mathrm{I}^\bullet$) may form iodine complex (I-M) with the monomer by a coordination bond. The functional monomers have coordination groups (*N,N'*-dimethylamino, ethylene glycol and glycidyl) to combine temporary with these organoiodine species, and the activation of the C-I bond of the light sensitive dormant species was subsequently promoted under visible light irradiation with the help of specific monomers (DMAEMA, PEGMA and GMA) to generate active propagating radicals (Polymer$^•$) and iodine radicals (I$^•$). The propagating radicals (Polymer$^•$) can then trigger chain growth, contributing to high initiation efficiencies and high monomer conversions in a relatively short period, and I$^•$ and Polymer$^•$ could also deactivate to alky iodine dormant species, which establish the activation-deactivation equilibrium and contribute to control/"living" features of the polymerization system (Fig. 2b).

In particular for the bulk polymerization of PEGMA, as an unstable radical, I$^•$ was inclined to self-terminated to provide iodine molecular (I_2) accumulated in the polymerization system, as detected by a reddish-yellow colour and characteristic absorption peaks at 365 and 297 nm in the UV-vis spectra (Fig. S11). Meanwhile, the probability of coupling termination of polymer radicals to give dead polymers increased due to the loss of opportunity to form dormant species with I$^•$, which may introduce bimodal curves in GPC analysis. Although the polymerization exhibited good molecular weight distribution control and normal distribution single curve at low monomer conversions, GPC curves possessed double peaks as the monomer conversion increased due to the formation of high molecular weight polymers from the radical-coupling (RC) reactions of polymer-end radicals. When the similar molecular weight was achieved, the incidence of the emergence of the RC is different between the polymerization systems at ratios of 100: 1 and 50:1 ($[PEGMA]_0$:$[CP\text{-}I]_0$). In the polymerization system at DP of 50, a double peak phenomenon was observed when the molecular weight rose to M_n = 16040 g mol^{-1} (M_w/M_n = 1.09) with monomer conversion of 71.9%, while still no obvious coupling termination occurred at DP of 100 to the similar molecular weight (M_n = 17970 g mol^{-1}, M_w/M_n = 1.09, conv. = 44.6%). We can infer that RC reaction is determined by the reaction component ratio and the molecule collision probability within the polymerization system. As polymers were obtained with similar molecular weights, the higher the system viscosity, the greater the probability of the RC reaction and doublet chromatographic peak profile in GPC curves. Unlike polymerizations of PEGMA, polymer distributions and GPC peak shapes were controllable and satisfying in the situation of DMAEMA and GMA polymerizations. A neat illustration of this phenomenon could be provided by UV-vis spectral analysis, and almost no accumulation of I_2 in DMAEMA and GMA polymerization systems resulted in rather less coupling termination of Polymer$^•$, which was in sharp contrast to that of the PEGMA polymerization system. So it is hardly surprising that monomodal distribution curves were obtained for bulk polymerization of DMAEMA or GMA, and higher conversions can be achieved in a relatively short period of time. The UV-vis spectra exhibited that the absorption of the polymerizations system located in the wide visible light scope extended to about 650 nm, further confirming that the successful LRP could be realized under various types of visible light irradiation.